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A Comparative Study of Alkoxysilanes and Acrylics in Sequence and in Mixture

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An experimental programme was designed to quantify differences in the physico-mechanical properties of models that were caused by the application of acrylic and silane in sequence, rather than in mixture. Test results indicated that the method of application did not cause great differences in most properties of the treated models, but that mixtures were somewhat more effective. Based upon these results, and the treatment requirements of the column, the limestone was treated with a sequential application of an acrylic resin and an alkyl alkoxysilane.

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Contents

Editorial	
DAVID WATT	5
Propping Up Pisa – Part One	
JOHN B. BURLAND	7
A Comparative Study of Alkoxysilanes and Acrylics in Sequence and in Mixture	
FRANK G. MATERO AND ANNE B. OLIVER	22
The Conservation of Singapore's Chinatown	
SIM LOO LEE	43
The Susceptibility of Historic Brick Masonry to Decay	
S. PAVÍA SANTAMARÍA AND J.R. BOLTON	58
The Conservation of Monasteries in the Western Himalayas	
JYOTI P. SHARMA AND JANHWIJ SHARMA	68
Book Reviews	85
Forthcoming Events And Notices	93

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FRANK G. MATERO AND ANNE B. OLIVER

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Introduction

Mission San José y San Miguel de Aguayo was founded in 1721, in what is now San Antonio, Texas, USA, by the Franciscan brothers of the College of Zacatecas, Mexico. An extensive rebuilding programme was undertaken in the 1770s, resulting in many of the elements of the church and Convento complex standing today. The rubble walls of the buildings were constructed mainly of local tufa and sedimentary lime-

stone, laid in and stuccoed with lime mortar; decorative elements were sculpted from a softer and more compact white limestone.

By the 1820s, the mission was nearly abandoned; by the 1850s it was considered a picturesque ruin by tourists and photographers. In 1861, the church and Convento were reinhabited by brothers of the Benedictine order, and a programme of rebuilding was begun using locally available materials. Most of the new elements were rubble limestone laid in lime mortar, with one exception – the carved, octagonal drums of a limestone column were laid in gypsum mortar. The column was intended to accent the second storey of an interior stair hall in the Convento; in 1868, however, the Benedictines left the site without completing their renovation, and the Convento was never roofed.

The mission complex was again largely abandoned until the 1920s, when renewed interest in all of the San Antonio missions resulted in extensive archaeological investigation, reconstruction and maintenance of the structures. In conjunction with these efforts, the Convento of Mission San José was stabilized and the column bears the evidence of two repair campaigns. The first is revealed in a photograph from around 1927 in which large white patches are visible; these matched the locations of present-day gypsum repairs. The second set of repairs were applied at an undetermined later date, and appear in photographs dating from the 1960s; these are of lime and sand, and overlay the earlier gypsum repairs and original gypsum bedding mortar (Figure 1).

In 1978, San Antonio Missions National Historical Park was established, of which Mission San José is a part. Since 1987, the increasingly rapid deterioration of the column in the Convento has been monitored by the National Park Service, leading to the decision to conserve the column in the spring of 1993.¹

Pre-treatment conditions

In plan, the column is an elongated octagon, approximately 18 in. on its east-west axis and 24 in. on its north-south axis. It is composed of nine drums reaching a height of 7 ft 10 in.; the first seven drums from the base are carved from a golden-brown limestone, and the eighth from a weaker grey limestone. The ninth drum forms a simple capital, and is also of a golden-brown limestone. Petrographic analyses of weathered samples of the golden-brown stone identified it as an impure limestone, composed of a high percentage of angular grains of

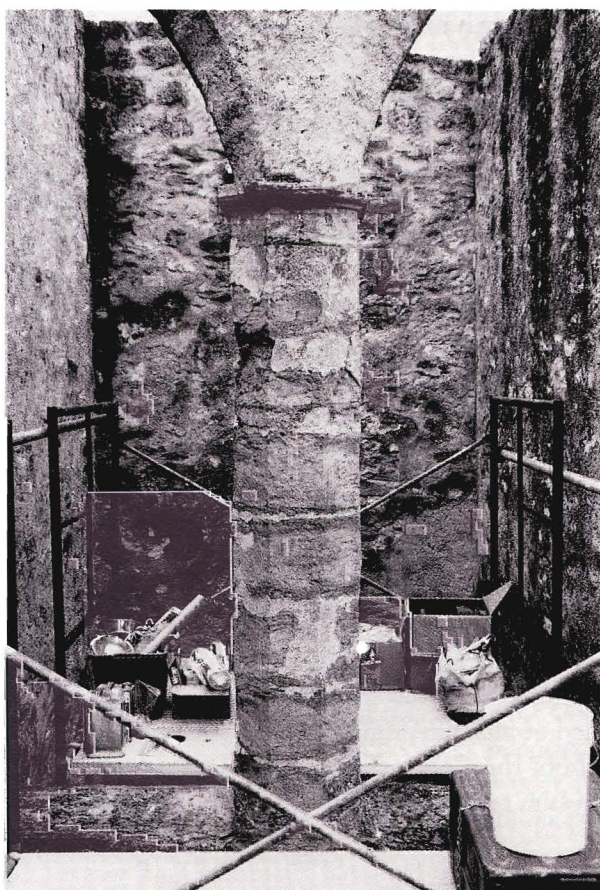


Figure 1
*South elevation of
Convento column
before conserva-
tion (1993).*

quartz in a cryptocrystalline calcite matrix; lesser amounts of clay and iron oxide minerals were also present.^{2,3} Tests for anions revealed a high concentration of sulphates (SO_4^{2-}) in the stone.² Although the high sulphate content may have derived in part from the mineralogical composition of the stone, its probable source was the bedding and repair mortar used on the column (see below).

The white bedding and repair mortar was identified as calcium sulphate (CaSO_4), or gypsum.² Gypsum is a water-soluble salt; upon exposure to exterior weathering conditions, such as rain and snowmelt, the gypsum may move into solution as SO_4^{2-} and permeate the stone. With the evaporation of the atmospheric water, the SO_4^{2-} will recrystallize within the pores of the stone as gypsum or as other hydrated sulphates, exerting pressure on the walls of the pores and eventually causing the

development of cracks. These new cracks facilitate the further ingress of water and solubilized salts. The presence of clays and iron oxides in the mineralogical composition of the stone may also be contributing to deterioration. In the presence of water, some clays swell and may exert pressure within the stone pores. In like manner, ferrous ions may change oxidation states in the presence of water; the crystal structure of the new oxides may take up more volume than the original oxides.

The condition of the column prior to conservation was quite poor. Levels of deterioration were localized, such that sound surfaces were interspersed with deteriorated surfaces. The southern faces of the column were relatively sound, as were isolated areas on other faces. No gypsum was used on or above the capital of the column and this drum was in excellent condition. Sound surfaces did not require any consolidative treatments, but would benefit from the application of a water repellent.

The most severe deterioration was located in areas immediately beneath and adjacent to gypsum mortar and repairs; stone in these areas was very friable to the touch and exhibited the extensive micro-cracking and flaking typical of salt-contaminated stone. Many repairs of lime and gypsum rang hollow when tapped, indicating poor attachment to the underlying stone. When these repairs were subsequently removed, the stone beneath was found to be severely deteriorated (Figure 2). The deteriorated areas displayed excessive friability (loss of intergranular cohesion) to a depth of up to 5 cm, as well as flaking (delamination) of larger fragments of stone. These two types of deterioration required two types of treatment: a deeply-penetrating consolidant to re-establish intergranular cohesion, and an adhesive to restore cohesion between larger grains and to bridge the gaps between large flakes caused by microcracking.

Finally, because the column is an exterior, load-bearing, architectural element, water could not easily be removed from the system, nor could all of the gypsum be removed without dismantling the column. Thus a third treatment was required: the application of a protective, water-repellent coating.

Proposed column treatment programme and selection of treatments

The development of a treatment programme for the limestone column was based upon the petrographic characterization of the stone, a

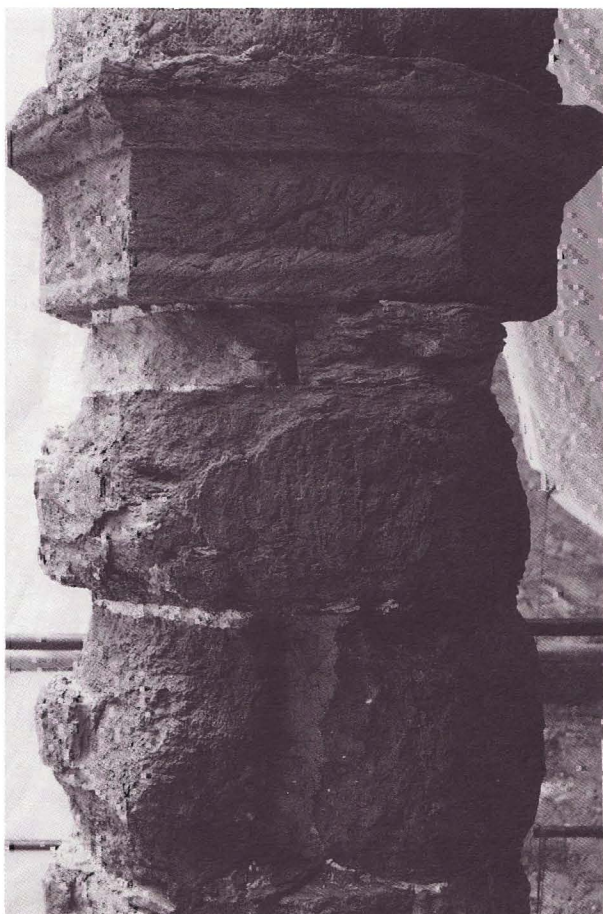


Figure 2
Top of east
elevation of
Convento column
after removal of old
repairs and before
conservation
(1993).

condition survey that mapped the types and extent of deterioration on the column,³ and on information derived from an extensive literature review.⁴ Based upon this information, the application of a mixture of an acrylic and a silane would seem the most effective treatment for the conservation of the column, but three considerations countered the use of a mixture:

- The reported depth of penetration of acrylic-silane mixtures was not adequate for the most severely deteriorated areas of the column. Reports on the consolidative abilities of silanes alone were too variable, while acrylics alone did not possess adequate depths of penetration. In contrast, ethyl silicate has an excellent record of both deep penetration and good intergranular consolidation.

- The deterioration of the column was quite localized, and in sound areas it was not appropriate to introduce the adverse effects of colour change and reduction of water vapour permeability caused by acrylics.^{5,6} The sound areas would, however, benefit from a protective, water-repellent coating.
- After consolidation, large areas of loss were designated to be infilled with a hydraulic lime-based repair mortar, to restore the visual coherence and the structural integrity of the column. While it was necessary to stabilize the friable and flaking surfaces with both a consolidant and an adhesive prior to infilling, a hydrophobic surface would interfere with the adhesion of the repair mortar. The incorporation of epoxies or acrylics in the mortar would allow for successful application over a water-repellent surface.⁷ These organic resins are, however, susceptible to degradation by ultraviolet radiation, and such repairs would be difficult to remove or replace in the future.

Thus it was proposed to apply an ethyl silicate consolidant to the entire column, an acrylic adhesive to all friable areas, hydraulic lime-based repair mortar in designated areas, and, finally, alkoxysilane water repellent to the entire column. This sequential application of the consolidant, adhesive and water repellent was considered more practical, flexible, and potentially more effective than the application of a mixture. No comparative studies or treatment reports were, however, found on the effects or effectiveness, if any, of applying the acrylic and silane to stone in a series of steps, as opposed to a single mixture.

The experimental programme that follows was designed to begin to compare the differences in the physical and mechanical properties of stone, if any, which were caused by sequential and mixed applications of alkyl alkoxysilanes and acrylics.

Experimental programme design

Because of the small size, visibility and structural importance of the column, it was not possible to obtain weathered samples of the stone for testing. Instead, models were used in the experimental programme; these were made from equal parts of angular quartz sand and marble dust, a chemically stable form of calcium carbonate. Water was added until the mixture was of a plastic consistency, or about 15 per cent by weight of the dry ingredients. The mixture was placed in moulds to

form disks that were $2\frac{3}{4}$ in. in diameter and $\frac{3}{4}$ in. high (for use in the water vapour transmission test) or 2 in. cubes (for use in all other tests). The disks and cubes were allowed to set in the moulds for 12 to 24 hours, and were then placed in a $60\pm5^{\circ}\text{C}$ oven to dry for 48 hours. Cohesion of the models relied primarily on mechanical bonds, rendering them quite weak and susceptible to weathering, and ultimately allowing for measurable results.

It must be emphasized that the models were in no way intended to replicate the chemical or physical properties of the limestone, and the quantitative results of the experimental programme cannot be inferred to correlate directly to the column stone. But certain advantages were derived from treating and testing the models, rather than the stone samples. The primary purpose of the experimental programme was not to measure the effectiveness of the individual treatments in consolidating the substrate, but to measure the interactions and effects of the treatments upon each other, which thereby influenced their effectiveness in consolidating the substrate. And because the same treatments were applied to all of the models, the method of their application was the only variable. The models were more homogeneous in composition than the stone samples, and variations in the test results of different treatment groups could be assumed to be caused by the interaction of the treatments with each other, rather than by heterogeneities in the substrate; the homogeneity of the models also allowed for more statistically comparable test results. Thus, although the quantitative results of the experimental programme cannot be applied to the column, qualitative comparisons of the relative effectiveness of the two methods of application, as a result of their interaction, can be made. The information derived from these comparisons is valid not only for the specific instance of the limestone column, but for the general conservation of stone.

To compare the effects of applying acrylic and silane in sequence and in mixture, three products were applied to the models: Conservare Stone Strengthener OH, an ethyl silicate (ES), was used as the consolidant; Acryloid B72, an ethyl methacrylate/methyl acrylate copolymer (EM/MA), was used as the adhesive; and Dow Corning Silane Z6070, a methyl trimethoxysilane (MTMOS), was used as the water repellent.⁸ The models were divided into four treatment groups and given two-letter codes:

- CT – no treatment, acting as control.

- ES – treatment with ethyl silicate only.
- SQ – treatment with ES, followed by an application of a 5% w/v solution of EM/MA in toluene, followed by an application of undiluted MTMOS.
- MX – treatment with ES followed by an application of a mixture of 5% w/v EM/MA dissolved in undiluted MTMOS.

Treatments were brush-applied to the models designated for the depth of penetration test. All other models were treated by partial immersion; the treatments rose by capillarity until complete saturation was obtained. After each treatment, the models were placed on wire racks, which were loosely draped with plastic sheeting to prevent rapid evaporation of the solvents while allowing for sufficient air circulation; the models cured at ambient indoor temperature and humidity. After treatment with ES, all models cured for 14 days under controlled conditions. The SQ samples were then cured for four days after treatment with EM/MA and for seven days after treatment with MTMOS. The MX samples were cured for 14 days after treatment with the EM/MA and MTMOS mixture. The water vapour transmission test was begun immediately after cure, while all other samples were allowed to cure in ambient conditions for at least seven more days prior to testing.

Tests were selected to measure the physical and mechanical properties of the models after treatment, and were based on standardized procedures whenever possible. These tests measured the depth of penetration and the microstructure of sequences and mixtures of EM/MA and MTMOS, as well as changes in water absorption, bulk specific gravity, water vapour permeability, and resistance to salt crystallization of the individual models. To comply with testing standards, and to increase statistical accuracy and significance, four models from each treatment group were used whenever possible, totalling 16 samples per test. Because the CT models were water-soluble, untreated controls could not be used for the salt crystallization, water absorption, and bulk specific gravity tests. Instead, models treated with ES only were used as controls, thus totalling 12 samples per test.

Experimental programme results

Depth of penetration⁹

To be effective and to prevent the formation of a surface crust, a conservation treatment must penetrate through the deteriorated or altered zone and into the sound core of the stone. The purpose of this

test was to measure the depths of penetration of three separate brush-applied treatments (ES, SQ and MX), and to determine whether statistically significant differences existed between the depths of penetration of the three treatments.

Based upon a comparison of the means, the conservation treatment method involving the application of ES, followed by the application of a mixture of EM/MA and MTMOS, achieved the deepest penetration in the models (Table 1). The differences between the depths of penetration of ES and MX, and between SQ and MX, also proved to be statistically significant, while no significant difference existed between ES and SQ. Based upon these results, a mixture of EM/MA and MTMOS could be recommended over the sequential application of the same products; it is worthy of note, however, that the mean depths of penetration of all three treatments were much less than the depth of approximately 25–50 mm recommended in the conservation literature.

Because the ES cured fully before the application of either the sequence or the mixture, the solvents (toluene and methanol) used as the carriers for EM/MA and MTMOS should have had no effect on the ES (e.g. resolubilizing and thus redistributing the ethyl silicate). Thus the increased depth in penetration of the mixture is the result of the increased penetration of EM/MA dissolved in MTMOS.

Past studies indicated that the addition of EM/MA to MTMOS either did not affect or actually increased the depth of penetration of the latter, which at first seems contradictory.^{10,11} The viscosity of MTMOS is very low, allowing for potentially excellent depth of penetration, but its volatility is high and much evaporative loss can occur in the initial stages of polymerization. Logically, the addition of the large acrylic molecules would be thought to decrease the depth of penetration of the MTMOS, but it does not. This may be because the EM/MA 'entraps' the MTMOS within the acrylic polymer network, thus preventing evaporative loss of the highly-volatile silane and promoting its condensation in the stone. By this means, the initially good depth of penetration of MTMOS, although somewhat reduced by the addition of EM/MA, is maintained to some degree.¹² The above test results seem to support this observation, and also indicate that, in a sequential application, the polymerized EM/MA does not 'entrap' the MTMOS or cause a similar increase in depth of penetration.

A Comparative Study of Alkoxysilanes and Acrylics in Sequence and in Mixture

TEST	TREATMENT			
	Control (CT)	Ethyl Silicate (ES)	Sequence (SQ)	Mixture (MX)
Depth of Penetration depth (mm) increase	-----	2.43 0.0%	2.53 4.0%	2.88 16.0%
Water Absorption absorption (weight %) decrease	-----	7.20 0.0%	0.38 95.0%	0.30 96.0%
Bulk Specific Gravity bulk specific gravity increase	-----	2.10 0.0%	2.14 1.9%	2.19 4.3%
Water Vapour Transmission rate [g/(hr)(m ²)] decrease	7.67 0.0%	4.33 44.5%	2.15 72.0%	2.54 66.9%
Salt Crystallization weight loss (% original wt.): after 15 cycles after 18 cycles	----- -----	100.0% 100.0%	9.5% 28.4%	8.9% 41.2%

Control (CT) = untreated models

Ethyl Silicate (ES) = models treated with ethyl silicate only

Sequence (SQ) = models treated with ES, 5% EM/MA in toluene, and undiluted MTMOS

Mixture (MX) = models treated with ES, and 5% EM/MA dissolved in undiluted MTMOS

Table 1 Experimental programme results. Control models were water soluble, thus ethyl silicate models served as controls in experiments that required immersion. Values are based on the mean of four samples for each treatment group.

Microstructure¹³

Uneven deposition, reverse migration, or segregation of the EM/MA and MTMOS would create potential sources of weakness and lead to the eventual failure of a treatment. Of greatest concern would be the deposition of the EM/MA consolidant only on the surface of the treated substrate. In this event, an artificially strong crust would overlay unconsolidated material; the segregated layer of EM/MA might also inhibit water vapour transmission, and the recrystallization of soluble salts would take place behind the surface crust in the weaker layer, eventually causing the crust to spall. The microstructure of the resultant polymer networks, particularly their continuity and the manner in which they bond with the substrate, also affects the short- and long-term performance of the conservation treatments.

Scanning electron microscopy (SEM) was used to characterize the microstructure and appearance of the untreated models and those treated with ES, EM/MA or MTMOS only.¹⁴ Once these visual references had been established, samples that had been brush-applied with ES and a sequence or a mixture of EM/MA and MTMOS were examined to compare the microstructures and any differences in film deposition and morphology resulting from the two methods of application. Neither EM/MA nor MTMOS, nor the method of their application,

should have had any effect on the inorganic SiO_2 matrix formed by the cured ES. Results are in the form of photomicrographs; only the SQ and MX results are reported here (Figures 3 and 4).

Based upon the observed quantity of material deposited on the models, treatments with mixtures of EM/MA and MTMOS could be considered more effective than treatments with sequences of the same. The heterogeneity of the SQ film, and the contrasting homogeneity of the MX film, is a function of quantity, rather than of any visible segregation or irregular deposition of the two materials. Wheeler *et al*¹² found that when EM/MA and MTMOS were applied in a mixture, the EM/MA 'entrapped' the MTMOS material, preventing its evaporative loss and promoting condensation at later stages of polymerization. From the above images, it would appear that cured EM/MA does not entrap the MTMOS material.

One major difference in the application of EM/MA and MTMOS in sequence versus mixture is that toluene is used to dissolve the EM/MA in the sequential application, while the methanol intrinsic to the MTMOS is used to dissolve the EM/MA in the mixed application. The vapour pressure of methanol (95 mm Hg at 20°C) is higher than that of toluene (22 mm Hg at 20°C). Although EM/MA entraps MTMOS at later stages of polymerization, the presence of EM/MA in the MTMOS solution has no effect on initial evaporative loss.¹² Methanol, the more volatile solvent, may reduce the dwell time and induce the reverse migration of the EM/MA/MTMOS mixture at initial stages of polymerization, resulting in an accumulation of MX at the surface of the treated object, the presence of which we may be observing in Figure 4.

In contrast, the lower volatility of toluene should allow for the deeper penetration of EM/MA in the first stage of the sequential application. Cured EM/MA, however, remains reversible in organic solvents. When MTMOS is applied to a surface previously treated with EM/MA, the EM/MA may be redissolved in the methanol solvent used to dissolve the MTMOS. This would induce the reverse migration and loss of both EM/MA and MTMOS as the methanol evaporates.

The latter hypothesis is supported by the results of the bulk specific gravity test, which indicates that considerably less EM/MA and MTMOS are deposited in SQ models than in MX models. The results of other tests, including the improved resistance of models treated with SQ to water absorption and to salt crystallization (see below),

indicate that more EM/MA and MTMOS are deposited on the models than is visible in the SQ photomicrographs. It should be noted that only the surface-layer microstructure of the SQ and MX models was examined, and that the microstructure may be different at greater depths. In addition, only one SQ sample was examined, and the average appearance of SQ treatments cannot be generalized from these images. While the appearance of the MX photomicrographs is consistent with other SEM images of EM/MA/MTMOS mixtures,^{10,16,17} no SEM examinations of sequential applications of EM/MA and MTMOS were found in the literature. Further research is required to fully understand the microstructure of sequential applications.

*Water absorption*¹⁸

Changes in water absorption provide a measure of the water repellency

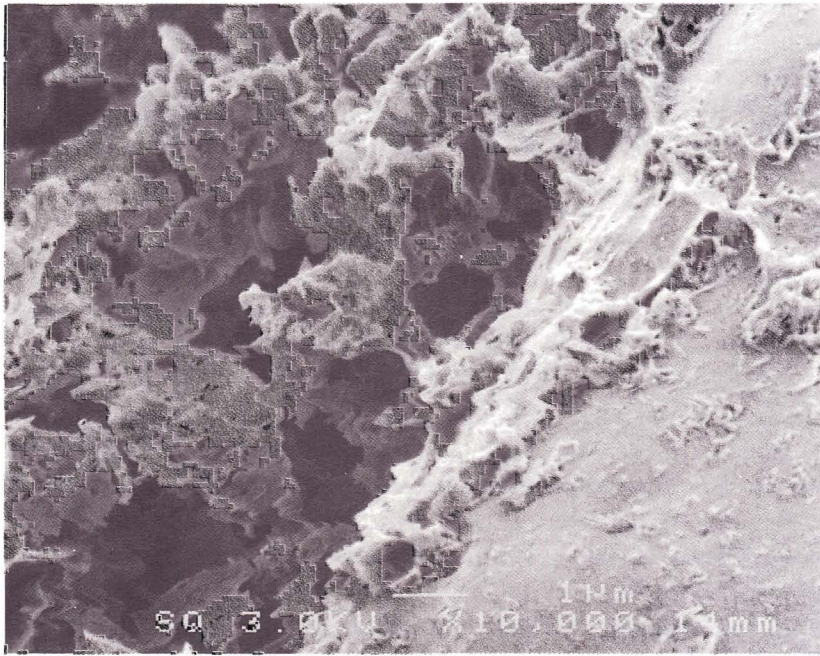


Figure 3 SEM photomicrograph of model treated with ES followed by sequential applications of EM/MA and MTMOS (SQ) and etched with 1M HCl (3.0KV, 10,000X magnification). In appearance, the microstructure of SQ is almost identical to the ES visual reference; it forms a glassy and discontinuous film. The presence of EM/MA and MTMOS is difficult to discern. The SQ appears less flat and more flexible than ES. Voids indicate the location of calcite grains prior to etching; few calcite grains are visible after etching.

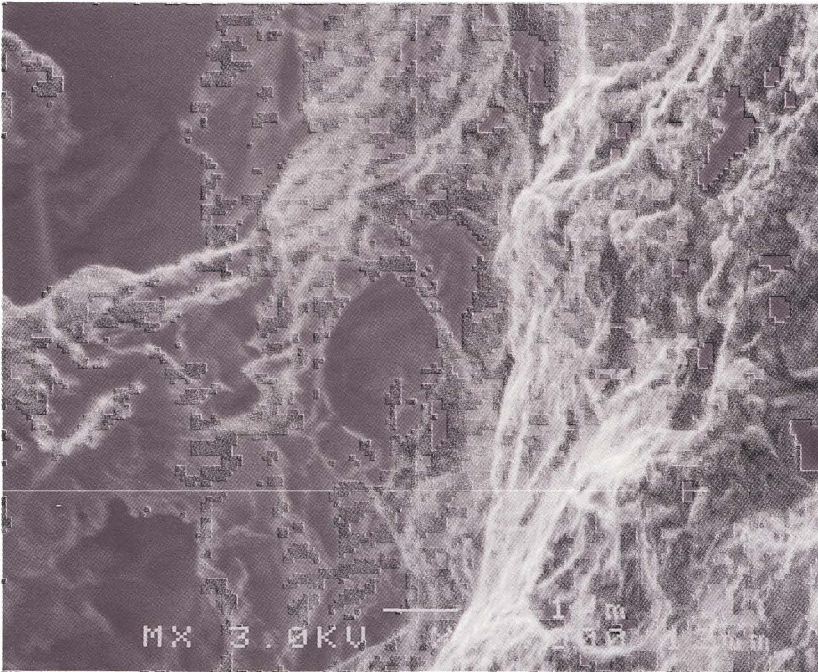


Figure 4 SEM photomicrograph of model treated with ES followed by a mixture of EM/MA and MTMOS (MX) and etched with 1M HCl (3.0KV, 10,000X magnification). In appearance, the microstructure of MX forms a thin and continuous film; the brittle and discontinuous ES pre-treatment is no longer visible and is presumably overlaid by the MX treatment. The smoothness and continuity of the film indicate the uniform dissolution of EM/MA in MTMOS, as does the somewhatropy nature of the film, visible as ridges around voids. Although these voids indicate that calcite grains were lost from the surface during etching, many others are still held within the MX matrix and are also visible in the layer immediately beneath the film. This physical 'locking-in' of calcite grains, for which MTMOS and EM/MA have no chemical affinity, was also observed by Charola et al.¹⁵

imparted by the conservation treatments. Water is the catalyst for most of the deterioration mechanisms affecting the stone of the Convento column, especially salt cycling, and a decrease in the water absorption of the treated surface correlates to an increase in water repellency, thereby limiting the presence of water in the system and reducing the potential for deterioration.

Although changes in absorption between two of the three treatment groups were not statistically comparable, a simple comparison reveals a tremendous decrease in the water absorption of models treated with SQ and MX (Table 1). From the per cent decrease in mean absorp-

tion it is apparent that both the SQ and MX treatments imparted a very high degree of water repellency to the models already treated with ES.

*Bulk specific gravity*¹⁹

The greater the amount of a conservation treatment absorbed by a material, the greater the effectiveness of that treatment. Changes in bulk specific gravity provided a measure of the retention of the conservation treatments. The models treated with MX displayed the greatest increase in bulk specific gravity, and thus the greatest per cent absorption of the EM/MA and/or MTMOS treatments (Table 1). As previously discussed, the polymer network formed by EM/MA may 'entrap' the MTMOS, preventing its evaporation, promoting *in situ* condensation reactions, and thus increasing the amount of MTMOS deposited in the samples. EM/MA is also known to significantly decrease the porosity of stone⁵; the capacity of the models to absorb MTMOS after the polymerization of EM/MA would be much reduced. These two factors may explain the lesser increase in bulk specific gravity exhibited by the SQ treatment group. Based upon these test results, a sequential application of EM/MA and MTMOS would not result in as high a per cent absorption of conservation materials, and would be less effective than a mixed application.

*Water vapour transmission*²⁰

When water is a principal agent in the deterioration of the stone, it is necessary to increase the water repellency of the stone if water cannot be removed from the deterioration cycle. But it is equally necessary to ensure that any water that does enter the stone, whether by direct contact or condensation, is also able to evaporate. Water trapped within the stone will facilitate water-related weathering and hasten the deterioration of the stone. Thus the lesser the decrease in the water vapour transmission rate, the more easily water and water vapour will exit, and the better the conservation treatment.

Although some of the data was not statistically comparable, a simple comparison of the means reveals that all of the treatments, ES, MX and SQ, affected the water vapour transmission rate of the models. Indeed, the decreases in water vapour transmission were quite large and well above any recommended limits for conservation materials (Table 1). Other studies indicate, however, that when these materials are applied to natural stone, which can be assumed to have greater

heterogeneity in pore size and structure than the models, decreases in water vapour transmission occur at more acceptable levels.^{6,9} The significant differences between the ES group, and both the SQ and MX groups, indicated that ES was not solely responsible for the decrease, and that sequences and mixtures of EM/MA and MTMOS respectively contributed to the decrease in water vapour transmission by approximately 75% and 50% of that caused by the ES alone.

Of greatest interest in this test was that the decreases between water vapour transmission rates caused by the method of treatment, namely the application of EM/MA and MTMOS in sequence or in mixture, statistically showed no significant difference. On the basis of this test, a sequential application could be considered as effective as a mixture.

Resistance to salt crystallization²¹

Intrinsic salts were identified as the primary cause of deterioration of the Convento column stone, but their complete removal from the system was not practicable. An effective conservation treatment would inhibit salt cycling or would allow for the removal of salts after treatment. In the long term, the treatment would also have to perform well in the presence of ongoing cycling by providing improved intergranular cohesion and microcrack adhesion.

Models treated only with ES were destroyed by repeated immersions in the salt bath after only eight cycles, although they displayed marked improvement over untreated CT models, which disintegrated upon contact with water. In contrast, the per cent weight loss for groups treated with SQ and MX was very minimal through cycle 15, and the ultimate destruction of the models was much slower than that of the ES or CT groups. In part, this may be a result of the consolidating properties of ethyl silicate (as observed in the improved resistance of the ES group over the CT group) and EM/MA. The addition of the water-repellent (MTMOS), however, reduced absorption of water by about 95 per cent. By drastically reducing the presence of the catalyst (water) in the salt crystallization cycle, the MTMOS limited the extent of salt solubilization and recrystallization, and possibly even delayed its inception. Thus the excellent resistance of the SQ and MX groups to destruction by salt cycling was probably a result of the addition of the water repellent to the conservation treatments.

Based upon the results of this test, it appears that no significant differences in the resistance of the models to salt crystallization are caused by the use of EM/MA and MTMOS in sequence, as opposed to

mixture. The dramatic increase in resistance of both the SQ and MX groups over that of the ES group, however, provides a strong argument for the use of EM/MA and MTMOS in conservation treatments where salt cannot be removed from the affected stone. This increase in resistance is most likely a result of the water-repellent properties imparted by the MTMOS and to a lesser extent the consolidating properties of the EM/MA. The exact contribution of each conservation material to the improved resistance cannot be determined without further testing.

Conclusions and recommendations for research

The results of the experimental programme revealed several significant differences between untreated models, models treated with sequences, and models treated with mixtures. A comparison between untreated and treated groups revealed that both methods of application caused a decrease in water vapour transmission rates, but greatly reduced water absorption rates and increased resistance to salt crystallization. A comparison between the two methods of application revealed that the mixture of EM/MA and MTMOS exhibited a greater mean depth of penetration than the sequence, that the microstructures of the two treatment methods differed, and that models treated with a mixture exhibited a greater mean increase in bulk specific gravity than models treated with a sequence. No significant differences in water absorption, water vapour transmission or resistance to salt crystallization existed between the sequential and mixed application methods. Based upon these results, the effectiveness of a mixed application of EM/MA and MTMOS was felt to be slightly better than that of a sequential application.

Further experimentation would help to clarify differences in the effectiveness of sequential and mixed applications of acrylics and silanes. Tests already conducted in this programme could be made relevant for specific types of stone by applying them to weathered stone samples, rather than to models. Other tests that were not included in this experimental programme would also help to evaluate the relative effectiveness of sequential and mixed applications of EM/MA and MTMOS. By testing the abrasion resistance, compressive and tensile strength, and modulus of rupture of treated samples, the consolidating effects of sequences and mixtures could be compared. Exposure to ultraviolet radiation and/or acid fog would reveal if any differences in ageing were caused by the method of application and the resultant dif-

ferences in morphology of sequences and mixtures of EM/MA and MTMOS.

Examination of different layers of the treated samples using SEM might reveal whether any segregation or separation of the two elements was caused by either method of application. The examination of samples at each stage of a sequential treatment would also reveal to what extent the treatments affected each other. Gas chromatography could be used to characterize the chemical interactions of EM/MA and MTMOS when applied in a sequence, similar to the way in which Wheeler *et al*¹² characterized the chemical interactions of EM/MA and MTMOS when applied in mixtures. Using this technique, one could determine whether EM/MA is resolubilized and lost to evaporation when MTMOS is applied as the second step in a sequence, and also whether MTMOS is 'entrapped' by the cured EM/MA and/or to what extent MTMOS too is lost to evaporation.

Column treatment programme

The conclusions of the experimental programme were considered in combination with the localized deterioration patterns and other treatment requirements of the column. A sequential application of the consolidant, adhesive and water repellent was considered more practical, flexible, and potentially more effective than a mixed treatment under these particular circumstances. In support of its selection was the fact that, in deteriorated areas designated for aesthetic and structural infill, the application of the acrylic would not be followed by the application of a water repellent; instead infills would be applied directly over the consolidated surfaces, and then the water repellent would be applied. This method would also eliminate the reduction in EM/MA and MTMOS deposition found to be caused by a sequential application. Thus, the following sequential treatment programme was implemented for the conservation of the Convento column at Mission San José:

- Pre-consolidation of extremely fragile surfaces and application of wet-strength tissue paper to vulnerable flakes using EM/MA (7.5% Acryloid B72 in 1:1 toluene:xylenes) to allow for both re-attachment of larger fragments and desalination without further loss of material.
- Mechanical removal of all lime-based and gypsum-based repairs.

- Re-attachment and filling of large voids behind detached fragments using a hydraulic lime-based grout.²²
- Desalination of salt-contaminated areas with repeated applications of a paper poultice and water.
- Application of an ethyl silicate consolidant (Conservare Stone Strengthener OH) to all surfaces of the column.
- Application of an EM/MA adhesive (3.75–7.5% Acryloid B72 in 1:1 toluene:xylenes) to selected areas exhibiting friability and microcracking.
- Application of recessed infills, composed of 1 part hydrated hydraulic lime, 3 parts quartz sand, and masonry pigments, to restore the structural and visual integrity of the column.²³
- Application of an MTMOS water repellent (Dow Corning Z6070) to all surfaces of the column, including areas of infill.



Figure 5
South elevation of
the Convento
column after
completion of all
conservation
treatments (1993).

Since the completion of treatment in 1993 (Figure 5), maintenance inspections of the column have been conducted in 1994 and 1996. The results of RILEM water absorption tests indicate no change in the performance of the water repellent. There has also been no further loss of material, no additional accumulation of salts, and continued good adhesion of the hydraulic lime-based repair mortar.

Biography

Frank G. Matero BA, MSc

Frank G. Matero is Associate Professor of Architecture, Chairman of the Graduate Program in Historic Preservation, and Director of the Architectural Conservation Laboratory, University of Pennsylvania. He was formerly Assistant Professor and Director of the Center for Preservation Research at Columbia University (1981–90); Lecturer in architectural conservation at the International Center for the Study of the Preservation and the Restoration of Cultural Property (ICCROM), Rome (1988–present); and Architectural Conservator for the National Park Service (1979–81).

Anne B. Oliver BA, MSc

Anne Oliver is an architectural conservator in private practice. Since 1993 she has worked primarily at prehistoric and historic archaeological sites in the American south-west, developing and implementing preservation plans for both materials and sites.

Notes

- 1 The Architectural Conservation Laboratory of the University of Pennsylvania and the Southwest Regional Office of the National Park Service undertook this joint research, training and treatment programme, which was conducted under a co-operative agreement established in 1992 between the University and the National Park Service. Funding was provided by Los Compadres de San Antonio Missions National Historical Park, which secured a grant from the Marcia and Otto Koehler Foundation. Team members included the authors, as well as Jake Barrow, project co-director (National Park Service, Intermountain Cultural Resources Center); Keith Newlin, project intern (National Park Service, Denver Service Center); and Diana Motiejunaite, project intern (National Park Service, ICOMOS intern).
- 2 Correspondence between F. Gale, Project Research Co-ordinator, Masonry Stabilization Services Corporation, to B. Spears, Preservation Architect, San Antonio Missions National Historical Park, 5 February 1988.
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- 4 Brackin, A. E., *A Comparative Study of The Effects of Applying Acrylics and Silanes in Sequence and in Mixture, with a Case Study of the Column in the Convento of Mission San José y San Miguel de Aguayo, Texas*, unpublished thesis, University of

- Pennsylvania, Philadelphia (1994).
- 5 Laurenzi Tabasso, M., Mecchi, A.M., Santamaria, U., and Venturi, G., 'Consolidation of Stone I: Comparison between a Treatment with a Methacrylic Monomer and Corresponding Polymer', *Engineering Geology of Ancient Works, Monuments and Historical Sites*, Vol 2, 1988, pp. 933-938.
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- 7 Larson, J.H., 'A Museum Approach to the Techniques of Stone Conservation', *4th International Congress on the Deterioration and Preservation of Stone Objects*, 1982, pp. 219-237.
- 8 Conservare Stone Strengtheners OH is an ethyl silicate in methyl ethyl ketone and is manufactured by ProSoCo, Inc., PO Box 171677, Kansas City, KS, 66117; Acryloid B72 is an ethyl methacrylate/methyl acrylate copolymer with a 70:30 molar ratio and is manufactured by Rohm and Haas, Philadelphia, PA; Dow Corning Z6070 is a monomer of methyl trimethoxysilane and is manufactured by Dow Corning Corp., PO Box 997, Midland, MI, 48686-0997.
- 9 The depth of penetration test was based upon a procedure recommended by Weber, H. and Zinsmeister, K., *The Conservation of Natural Stone: Guidelines to Consolidation, Restoration and Preservation*, Expert-Verlag, Ehningen (1991), and modified by the authors.
- 10 Charola, A.E., Rossi-Manaresi, R., Koestler, R.J., Wheeler, G.E., and Tucci, A., 'SEM Examination of Limestones Treated with Silanes or Prepolymerized Silicone Resin in Solution', *Adhesives and Consolidants: Preprints of the Contributions to the Paris Congress, IIC Conference, Paris*, 1984, pp. 182-184.
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- 12 Wheeler, G.S., Shearer, G.L., Fleming, S., Kelts, L.W., Vega, A., and Koestler, R.J., 'Toward a Better Understanding of B72 Acrylic Resin/Methyltrimethoxysilane Stone Consolidants', *Materials Issues in Art and Archaeology II*, No 185, 1991, pp. 209-226.
- 13 Etching of samples for SEM with 1M HCl was based upon procedures used by Charola *et al.*¹⁰ and E. de Witte, A.E. Charola, and R.P. Sherry in 'Preliminary Tests on Commercial Stone Consolidants', *Vth International Congress on Deterioration and Conservation of Stone*, Vol 2, 1985, pp. 709-719, and modified by the authors.
- 14 This portion of the research was supported by the National Science Foundation MRL Program, under Grant No. DMR91-20668. The authors would like to thank Xue Qin Wang of the Laboratory for Research on the Structure of Matter, University of Pennsylvania, for her help.
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- 18 The water absorption test followed ASTM C 97 - 83 (reapproved 1983), *Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone*.
- 19 The bulk specific gravity test followed ASTM C 97 - 83 (reapproved 1983), *Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone*.
- 20 The water vapour transmission test followed ASTM E 96 - 90 (1990), *Standard Test Methods for Water Vapor Transmission of Materials, Water Method*.
- 21 The salt crystallization test followed ASTM C 88 - 90 (1990), *Standard Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate*, and RILEM 25 P.E.M. Test V.1b, *Crystallisation Test by Total Immersion (for Treated Stone)*.
- 22 Matero, F.G., and Bass, A., 'Design and Evaluation of Hydraulic Grouts for the Reattachment of Lime Plasters on Earthen Walls', *Conservation and Management of Archaeological Sites*, Vol 1 No 2, 1995, pp. 97-108.
- 23 The materials and methods of infill were based on the project's stated conservation objectives, which included visual re-establishment (not replication) of the column form, authenticity of original and repair materials given the uniqueness of the element and the ruin context, and reversibility and material compatibility of the infills.